Reduction of Aldehydes and Ketones by Transition-Metal Hydrides. 1. Reaction of *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ with Simple and Phenoxy-Functionalized Aldehydes and Ketones

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The reaction of *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ (1) with propanal and benzaldehyde yields unstable insertion products. The C=O double bond of salicylaldehyde rapidly inserts into the W–H bond of 1, affording the alkoxide **3a**. This compound readily isomerizes to the more stable phenolate **3b**. In the presence of excess salicylaldehyde **3a** and **3b** react further to the isolable tungsten salicylates **3c** and **3d**, respectively, with liberation of the organic reduction product α,2-dihydroxytoluene. Compound **3d** crystallizes in the monoclinic space group $P2_1/c$ with a = 8.863 (3) Å, b = 10.849 (3) Å, c = 19.939 (6) Å, β = 96.31 (2)°, V = 1905.7 (10) Å^3, Z = 4, and R = 0.0558 for 3402 observed reflections. In the solid-state structure of **3d** the salicylate moiety, acting as an O,O′-bidentate ligand to tungsten, shows some quinoid character. Similarly, 1 reacts with 2 equiv of 2-hydroxyacetophenone, producing 4 and 1-(2-hydroxyphenyl)ethanol. Treating 1 with methyl salicylate affords **5**, albeit via a simple acid–base reaction with evolution of H_2. Reaction of 1 with 4-hydroxybenzaldehyde initially yields the insertion product **6a**, after which an equilibrium reaction between different tungsten phenolates sets in.

Introduction

Main-group hydrides are common reagents for the reduction of aldehydes and ketones to alcohols.[1] High selectivities have been achieved by sophisticated, complex hydrides of the type $MM'H_xR_{4-x}$ (M = group 1 element, M′ = group 13 element, R = alkyl, alkoxide, and/or amide group), exemplified by the well-known Selectride ($MBH(s\text{-}Bu)_3$) and Super-Hydride ($LiBHEt_3$). To date, the use of transition-metal hydrides for this purpose is very limited.[1] This can be attributed to the fact that they are not always attainable on a multigram scale, but also because their reducing power is generally less than that of the main-group hydrides. On the other hand, the reactivity and selectivity of transition-metal hydrides can be much more tuned than that of the main-group hydrides, due to the availability of a wide range of ligands with different σ-donating/π-accepting properties. Besides, these hydrides seem to be more suitable for kinetic and mechanistic studies, as has been demonstrated by Darensbourg et al. on the $HM(CO)_4(L)^-$ system (M = Cr, W; L = phosphine).[2]

We have shown that the complex *trans,trans*-$WH(CO)_2(NO)[P(OiPr)_3]_2$ easily reduces a great variety of aldehydes in the presence of a weak acid such as acetic acid or phenol.[3] The high reactivity of this complex in this reduction was attributed to the presence of a nitrosyl ligand trans to the hydride atom, causing a hydridic polarization of the W–H bond (the "nitrosyl effect"). Nevertheless, an acid is needed to activate the aldehyde, whereas ketones do not react at all with this tungsten complex. In the course of our investigations we found that the reducing power of these complexes may be further enhanced by the substitution of the phosphites by small alkylphosphine ligands, e.g. PMe_3 and PEt_3.[4] We therefore set out to investigate the reactivity of the complex $WH(CO)_2(NO)(PMe_3)_2$ toward a variety of aldehydes and ketones; the first results of this study are presented in this paper.

Experimental Part

All preparations were carried out under an atmosphere of dry nitrogen, by conventional Schlenk techniques. All of the described reaction products, however, could be handled in air. Solvents were dried and freshly distilled before use. *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ was prepared as described previously.[4a] IR spectra were recorded as toluene solutions on a Bio-Rad FTS-45 instrument. Mass spectra (EI) were run on a Finnigan MAT-8230 mass spectrometer; the major peaks given are based on ^{184}W. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 instrument operating at 200 and 50.3 MHz, respectively, and ^{31}P NMR spectra on a Varian XL-200 spectrometer at 81 MHz.

***trans*-W{OC$_6$H$_4$[2-C(O)H]}(CO)(NO)(PMe$_3$)$_2$ (3c,d).** A solution of *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ (0.15 g, 0.35 mmol) and 2.5 equiv of salicylaldehyde in 10 mL of toluene was stirred for 24 h at room temperature in vacuo. The resulting deep red-brown solution was then evaporated to dryness. The residue was vigorously shaken with water in order to remove all high-boiling organic materials. After subsequent washings with cold diethyl ether and hexane, a red-brown solid remained; yield 85%. MS: m/z 515 (M), 487 (M – CO), 411 (M – CO, PMe_3), 381 (M – CO, PMe_3, NO). IR: ν_{NO} 1583, ν_{CO} 1885 cm^{-1}. Anal. Calcd for $C_{14}H_{23}NO_4P_2W$: C, 32.64; H, 4.50. Found: C, 32.14; H, 4.39. Crystals of **3d** suitable for a single-crystal X-ray diffraction analysis were grown by slow diffusion of hexane into a saturated solution of the compound in toluene.

***trans*-W{OC$_6$H$_4$[2-C(O)Me]}(CO)(NO)(PMe$_3$)$_2$ (4). Method A.** 4 was prepared as described above using 2-hydroxyacetophenone instead of salicylaldehyde for 3 h at 50 °C; yield 80%. MS: m/z 529 (M), 501 (M – CO), 425 (M – CO, PMe_3), 395 (M – CO, PMe_3, NO). IR: ν_{NO} 1575, ν_{CO} 1882 cm^{-1}. Anal. Calcd for $C_{15}H_{25}NO_4P_2W$: C, 34.05; H, 4.76. Found: C, 34.40; H, 4.86.

(1) See e.g.: *Houben-Weyl Methoden der Organischen Chemie*; Georg Thieme Verlag: Stuttgart, Germany, 1981; Vol. IV/1d, pp 267–282, 293–338; 1984, Vol. VI/1b, pp 141–288.

(2) (a) Darensbourg, M. Y.; Slater, S. *J. Am. Chem. Soc.* **1981**, *103*, 5914. (b) Slater, S. G.; Lusk, R.; Schumann, B. F.; Darensbourg, M. *Organometallics* **1982**, *1*, 1662. (c) Gaus, P. L.; Kao, S. C.; Darensbourg, M. Y.; Arndt, L. W. *J. Am. Chem. Soc.* **1984**, *106*, 4752. (d) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428. (e) Tooley, P. A.; Ovalles, C.; Kao, S. C.; Darensbourg, D. J.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1986**, *108*, 5465.

(3) Kundel, P.; Berke, H. *J. Organomet. Chem.* **1987**, *335*, 353.

(4) (a) van der Zeijden, A. A. H.; Sontag, C.; Bosch, H. W.; Shklover, V.; Berke, H.; Nanz, D.; Von Philipsborn, W. *Helv. Chim. Acta* **1991**, *74*, 1194. (b) van der Zeijden, A. A. H.; Bosch, H. W.; Berke, H. *Organometallics* **1992**, *10*, 563.

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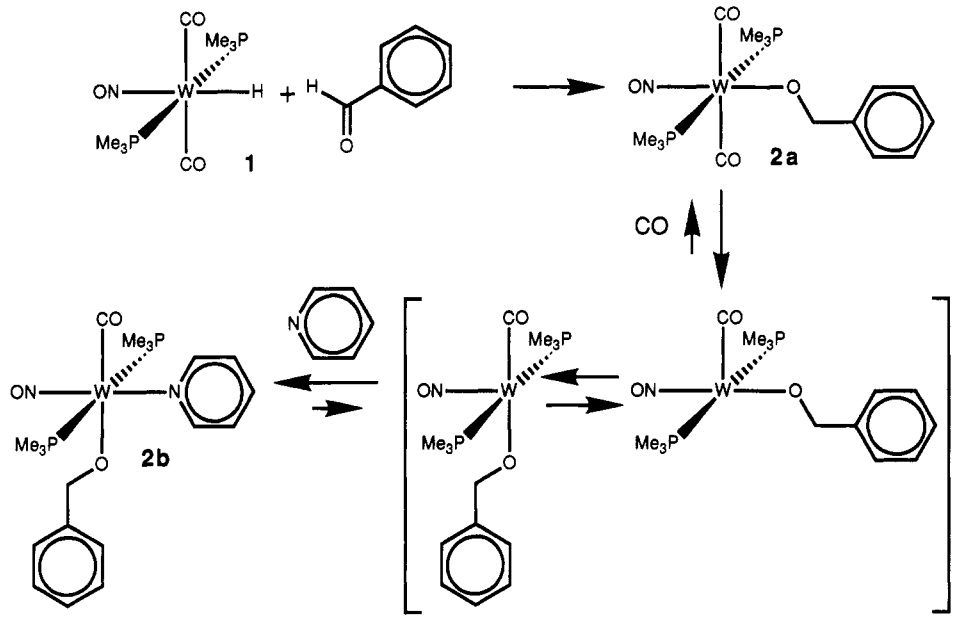
Scheme I



Method B. A solution of *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ (0.14 g, 0.33 mmol) and 0.10 mL (2.4 equiv) of 2-hydroxyacetophenone in 8 mL of hexane stood at room temperature for 3 days. A crop of red-brown crystals precipitated, which were filtered off and dried in vacuo; yield 45%.

***trans*-W{OC_6H_4[2-C(O)OMe]}(CO)(NO)$(PMe_3)_2$ (5).** A solution of *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ (0.38 g, 0.90 mmol) and 0.25 mL (2.5 equiv) of methyl salicylate in 15 mL of toluene was stirred for 24 h at 50 °C in vacuo. After the solvent was evaporated and the residue washed with water, the residue was extracted with hot hexane (3 × 25 mL). Chilling the combined extracts afforded a 80% yield of an orange-red powder. MS: *m/z* 545 (M), 517 (M − CO), 502 (M − CO, Me), 469 (M − PMe_3), 426 (M − CO, PMe_3, Me), 398 (M − 2CO, PMe_3, Me), 383 (M − 2CO, PMe_3, NO). IR: ν_{NO} 1579, ν_{CO} 1880 cm^{-1}. Anal. Calcd for $C_{15}H_{25}NO_5P_2W$: C, 33.07; H, 4.62. Found: C, 32.80; H, 4.63.

NMR Reactions and Kinetic Experiments. In a typical run 50 mg (0.12 mmol) of *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ was dissolved in 0.50 mL of C_6D_6 and the appropiate amount of reagent (propanal, benzaldehyde, salicylaldehyde, or 4-hydroxybenzaldehyde) was added by microsyringe. The NMR tube was then sealed and the mixture studied by ^1H, ^{13}C, and/or ^{31}P NMR spectroscopy. The NMR tube was left in the NMR machine during the entire experiment, whereas the temperature was calibrated against the known temperature-dependent ^1H resonances of methanol before running the experiment.

X-ray Analysis of 3d. A dark red crystal of dimensions 0.52 × 0.36 × 0.76 mm was sealed in a thin-walled glass capillary and mounted on a Siemens P3 diffractometer equipped with a graphite-monochromated Mo Kα X-ray beam. Cell constants and the orientation matrix were obtained and refined from the settings of 24 centered reflections in the range $10 < \theta < 20°$. Data were collected over the range $4 < 2\theta < 55°$ using the Wyckoff scan technique. Three reflections were checked every 97 measurements, showing no appreciable decay. Data were corrected for Lp effects, and a semiempirical absorption correction was applied. The tungsten atom was located from a Patterson search; the other non-hydrogen atoms were found from subsequent difference Fourier syntheses. Hydrogen atoms were fixed on idealized positions (d_{C-H} = 0.96 Å) and allowed to ride on their carrier atoms. All non-hydrogen atoms were refined anisotropically, and for the hydrogen atoms a common isotropic temperature factor was refined. During the final stages of convergence full-matrix least-squares refinement was applied. Calculations were performed using the SHELX package.[5] Further details of the crystal structure determination are given in Table I. A list of fractional coordinates is given in Table II.

(5) Sheldrick, G. M. SHELXTL-PLUS, Crystallographic System, Version 2; Nicolet XRD Corp.: Madison, WI, 1987.

Table I. Crystal Data for 3d

formula	$C_{14}H_{23}NO_4P_2W$	Z	4
mol wt	515.1	d_c, g/cm^3	1.795
cryst syst	monoclinic	μ(Mo Kα), cm^{-1}	63.71
space group	$P2_1/c$	temp, K	221
a, Å	8.863 (3)	no. of rflns	4904
b, Å	10.849 (3)	no. of unique rflns	4376
c, Å	19.939 (6)	no. of obsd rflns	3402
β, deg	96.31 (2)	($F > 6\sigma(F)$)	
V, Å^3	1905.7 (10)	no. of variables	201
		R, R_w values, %	5.58, 5.57

Results and Discussion

Reaction of $WH(CO)_2(NO)(PMe_3)_2$ (1) with Simple Aldehydes and Ketones. The tungsten hydride 1 reacts readily with propanal (minutes at room temperature) and benzaldehyde (hours at 50 °C). When the reactions were monitored by NMR spectroscopy in C_6D_6, a triplet signal at 3.42 ppm ($^3J_{HH}$ = 6 Hz) and a singlet at 4.41 ppm indicate the formation of the insertion products $W(OPr)(CO)_2(NO)(PMe_3)_2$ and $W(OCH_2Ph)(CO)_2(NO)(PMe_3)_2$, respectively. As anticipated,[2d,3,6] both reactions were significantly accelerated by the presence of phenol, producing $W(OPh)(CO)_2(NO)(PMe_3)_2$[7] and equimolar amounts of propanol or benzyl alcohol, respectively, as the final products. In contrast, no reaction of 1 with acetone and benzophenone was observed, even after prolonged heating at 50 °C.

It proved to be impossible to isolate the presumed insertion products as well as the tungsten phenolate, due to decomposition.[8] The instability of these compounds can be attributed to a strong cis-labilizing effect of the alk-

(6) (a) Grey, R. A.; Pez, G. P.; Wallo, A. *J. Am. Chem. Soc.* **1981**, *103*, 7536. (b) Ito, T.; Koga, M.; Kurishima, S.; Natori, M.; Sekizuka, N.; Yoshioka, K. *J. Chem. Soc., Chem. Commun.* **1990**, 988. (c) Gibson, D. H.; El-Omrani, Y. S. *Organometallics* **1985**, *4*, 1473.

(7) $W(OPh)(CO)_2(NO)(PMe_3)_2$: ^1H NMR (C_6D_6) δ 1.22 (t, 3.4 Hz, 18 H, $P(CH_3)_3$), 6.65 (m, 2 H), 7.2 (m, 3 H, Ph H's); ^{13}C NMR (C_6D_6) δ 18.0 (t, 12.8 Hz, $P(CH_3)_3$), 115.4, 119.8, 129.7, 167.1 (Ph C's), 210.5 (t, 6.5 Hz, W–CO); ^{31}P NMR (C_6D_6) δ −22.13 (s with 14% ^{183}W satellites, $^1J(^{31}P,^{183}W)$ = 289 Hz); IR (hexane) ν_{CO} 1934 (vs), 2016 (w), ν_{NO} 1618 (m) cm^{-1}.

(8) The related complexes $W(OR)(CO)_2(NO)[P(O\text{-}i\text{-}Pr)_3]_2$, with R = Me and Ph, are more stable, which is probably due to the more π-electron-withdrawing properties of the phosphite ligands in these complexes. See: Kundel, P.; Berke, H. *Z. Naturforsch.* **1987**, *42B*, 993.

Table II. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å²) for the Non-Hydrogen Atoms of 3d

atom	x/a	y/a	z/a	U(eq),[a] Å²
W	0.14100 (5)	0.25366 (4)	0.9541 (2)	0.0444 (1)
P(1)	0.3217 (3)	0.2549 (3)	0.0093 (2)	0.057 (1)
P(2)	−0.0217 (3)	0.2643 (3)	0.1881 (1)	0.0504 (9)
O(1)	0.264 (1)	−0.0027 (9)	0.1455 (5)	0.088 (4)
O(2)	−0.107 (1)	0.1342 (9)	0.0031 (5)	0.075 (4)
O(3)	0.0652 (8)	0.4356 (7)	0.0635 (4)	0.052 (3)
O(4)	0.3057 (8)	0.3536 (7)	0.1578 (3)	0.046 (2)
N	−0.006 (1)	0.1783 (8)	0.0400 (5)	0.050 (3)
C(1)	0.220 (1)	0.093 (1)	0.1262 (6)	0.058 (4)
C(2)	0.125 (1)	0.540 (1)	0.0771 (5)	0.052 (4)
C(3)	0.252 (1)	0.564 (1)	0.1222 (5)	0.042 (3)
C(4)	0.298 (1)	0.690 (1)	0.1311 (6)	0.053 (4)
C(5)	0.415 (1)	0.725 (1)	0.1749 (6)	0.054 (4)
C(6)	0.498 (1)	0.632 (1)	0.2149 (6)	0.058 (4)
C(7)	0.459 (1)	0.512 (1)	0.2083 (6)	0.052 (4)
C(8)	0.339 (1)	0.474 (1)	0.1619 (5)	0.042 (3)
C(9)	0.324 (2)	0.387 (1)	−0.0460 (8)	0.088 (7)
C(10)	0.516 (2)	0.235 (2)	0.0461 (9)	0.107 (8)
C(11)	0.291 (2)	0.129 (1)	−0.0495 (8)	0.097 (8)
C(12)	−0.150 (2)	0.394 (1)	0.1903 (7)	0.077 (6)
C(13)	0.081 (1)	0.267 (1)	0.2733 (6)	0.070 (5)
C(14)	−0.148 (2)	0.134 (1)	0.1900 (8)	0.076 (6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

oxy/phenoxy groups on the carbonyl ligands, probably leading to the formation of compounds with higher nuclearity. Darensbourg observed facile loss of CO from the analogous $W(OR)(CO)_5^-$ anion, producing tungsten carbonyl cluster compounds with bridging alkoxy groups.[9]

The lability of the CO ligands in the tungsten alkoxides was corroborated by an NMR experiment, in which the reaction of **1** with benzaldehyde was conducted in the presence of pyridine at 40 °C (see Scheme I). The rate of insertion seemed not to be influenced by the presence of pyridine, but instead of $W(OCH_2Ph)(CO)_2(NO)(PMe_3)_2$ (**2a**), a single new compound was observed by ^1H and ^{13}C NMR studies, which was spectroscopically identified as $W(OCH_2Ph)(CO)(NO)(pyridine)(PMe_3)_2$ (**2b**).[10] By comparison,[4b,11] the chemical shift of the CO ligand (243.48 ppm) is indicative of a trans-positioned O atom, which leaves the NO ligand trans to the pyridine ligand in **2b**. This is not the expected CO-substitution product, for which it may be anticipated that the benzyloxy group remain trans to the NO ligand as in **2a**. Although **2b** is stable for days in solution, all attempts to isolate it have been elusive so far, probably due to a still weak coordination of CO and/or the pyridine ligand.

Some conclusions can be drawn from the above observations: (1) (reversible) loss of CO from **2a** is very fast (since we actually cannot see **2a**, the rate of CO loss must be some orders of magnitude larger than that of the insertion reaction); (2) loss of CO from **2a** leaves an unsaturated intermediate, in which the benzyloxy group is able to isomerize quickly between the positions trans to the CO and NO groups; (3) since other isomers of **2b** are possible and obviously also accessible, the arrangement of ligands in **2b**, i.e. CO trans to alkoxy and NO trans to pyridine, must be thermodynamically the most stable one.

Table III. Kinetic Data for the Reaction of 1 with Salicylaldehyde[a]

[1], mol L⁻¹	amt of salicylaldehyde, equiv	solvent	k_1, M⁻¹ s⁻¹	10^4k_2, s⁻¹	10^4k_3, s⁻¹	3c:3d
0.24	1	C_6D_6	0.068	7.1		
0.28	2.5	C_6D_6		15	2.3	9:91
0.19	6.5	C_6D_6		11	3.3	8:92
0.16	18	C_6D_6		5.7	3.0	9:91
0.20	5	CD_3OD			13	9:91

[a] At 22 °C. For a definition of rate constants, we refer to Scheme II.

Reactions of 1 with Salicylaldehyde. In order to circumvent the instability problem concerning the CO ligands and to study this kind of insertion reaction in more detail, we contemplated the use of organic substrates bearing another functional group in addition to the C=O double bond. The main purpose of this other group should be the "trapping" of the initial insertion product by chelate coordination to the tungsten center. We therefore considered the use of salicylaldehyde, in which the phenolic OH group can serve not only as a chelating moiety but also as an intramolecular activator for the insertion of the carbaldehyde moiety.

We studied the reaction **1** with 1, 2.5, 6.5, and 18 equiv of salicylaldehyde in C_6D_6 at 22 °C by ^1H, ^{13}C, and ^{31}P NMR and/or IR spectroscopy (see Table III). As anticipated, the reaction with salicylaldehyde is extremely fast in comparison with that of benzaldehyde. When equimolar amounts of reagents are used, a plot of 1/[**1**] or 1/[salicylaldehyde] against time affords a linear relationship, indicating second-order kinetics. The second-order rate constant k_1 was calculated to be 0.068 M^{-1} s^{-1}, which means that within 1 min half of the reagents had reacted under these conditions.

The reaction initially yields the insertion product **3a** (see Scheme II), which was characterized spectroscopically.[12] This tungsten alkoxide could not be isolated, as it reacts further, mainly by isomerizing to the more stable phenoxy compound **3b**. Under equimolar conditions of **1** and salicylaldehyde, **3b** would principally be the final reaction product. However, in line with the aforementioned general instability of alkoxy/phenoxy compounds, **3b** could not be isolated, due to decomposition within hours, and had therefore to be characterized spectroscopically as well.[13] The **3a** to **3b** conversion follows first-order kinetics with $k_2 = 7.1 \times 10^{-4}$ s^{-1}, corresponding to a half-life for **3a** of 15 min. Therefore, an intramolecular rearrangement may be anticipated, possibly via heterolytic fission of the W–O bond and the saltlike intermediate A, as depicted in Scheme II.

Neither **3a** nor **3b** was found to form six-membered chelates, by extrusion of a CO ligand and concurrent coordination of the OH group. We think this is prevented by the strong intramolecular hydrogen bonding within the alkoxy/phenoxy moieties in **3a** and **3b**.

(9) (a) Darensbourg, D. J.; Sanchez, K. M.; Reibenspies, J. H.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 7094. (b) Darensbourg, D. J.; Mueller, B. L.; Bischoff, C. J.; Chojnacki, S. S.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 2418.

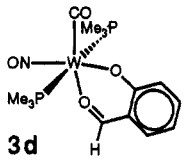
(10) Compound **2b**: ^1H NMR (C_6D_6) δ 1.08 (t, 3.0 Hz, 18 H, $P(CH_3)_3$), 5.16 (s, 2 H, OCH_2Ph), 6.69 ("t"), 7.30 ("t"), 7.49 (d), 9.44 (s, br) (aromatic H's, not all of which could be resolved or identified); ^{13}C NMR (C_6D_6) δ 14.6 (t, 12.1 Hz, $P(CH_3)_3$), 74.0 (OCH_2Ph), 126.0, 126.4, 128.2 (Ph C's, α-C not found), 124.3, 136.7, 149.3 (coordinated pyridine C's), 243.5 (t, 4.0 Hz, W–CO), free CO also observed (184.6 ppm).

(11) van der Zeijden, A. A. H.; Berke, H. To be submitted for publication.

(12) Compound **3a**: ^1H NMR (C_6D_6) δ 1.16 (t, 3.6 Hz, 18 H, $P(CH_3)_3$), 4.85 (s, 2 H, OCH_2–aryl), 6.73 (m, 2 H, aryl H), 7.04 (m, 2 H, aryl H), 11.7 (s br, 1 H, aryl OH); ^{31}P NMR (C_6D_6) δ −22.93 (s with 14% ^{183}W satellites, $^1J(^{31}P,^{183}W)$ = 287 Hz); IR (toluene) ν_{CO} 1930 (vs), 2011 (w) cm^{-1}.

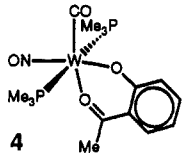
(13) Compound **3b**: ^1H NMR (C_6D_6) δ 1.11 (t, 3.7 Hz, 18 H, $P(CH_3)_3$, 3.95 (s, vbr, 1 H, aryl–CH_2OH), 4.27 (s, 2 H, aryl–CH_2OH), aryl H's 6.57 (d), 6.63 (t), 7.01 (m), 7.13 (d); ^{31}P NMR (C_6D_6) δ −21.69 (s with 14% ^{183}W satellites, $^1J(^{31}P,^{183}W)$ = 289 Hz); ^{13}C NMR (C_6D_6) δ 16.8 (t, 14.1 Hz, $P(CH_3)_3$), 64.9 (aryl–CH_2OH), 116.2, 117.8, 128 (?), 128.3, 131.4, 165.2 (aryl C's), 210.3 (t, 6.4 Hz, W–CO); IR spectrum coincides with that of **3a**.

Table IV. NMR Data[a]



3d

^{1}H: 1.00 (t, 3.4 Hz, P(C*H*3)$_3$), 6.32 (d × d, H$_4$), 6.72 (d, H$_6$), 6.84 (d × d, H$_3$), 7.03 (d × d × d, H$_5$), 8.93 (s, C(O)*H*), ^3J(H$_3$,H$_4$) = 8.1 Hz, ^4J(H$_3$,H$_5$) = 1.9 Hz, ^3J(H$_4$,H$_5$) = 6.6 Hz, ^3J(H$_5$,H$_6$) = 8.6 Hz
^{13}C: 14.2 (t, 12.6 Hz, P(*C*H$_3$)$_3$), 189.7 (*C*(O)H), 243.1 (t, 3.3 Hz, W-*C*O), 171.1 (C1), 124.3 (C2), 135.9 (C3), 115.4 (C4), 138.1 (C5), 123.9 (C6)
^{31}P: −10.34 (^1J(^{31}P,^{183}W) = 308 Hz)



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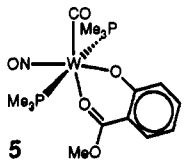
^{1}H: 1.02 (t, 3.3 Hz, P(C*H*$_3$)$_3$), 6.28 (d × d × d, H$_4$), 6.79 (d × d, H$_6$), 7.17 (d × d × d, H$_5$), 7.23 (d × d, H$_3$), 2.11 (s, C(O)C*H*$_3$), ^3J(H$_3$H$_4$) = 8.3 Hz, ^4J(H$_3$,H$_5$) = 1.8 Hz, ^3J(H$_4$,H$_5$) = 6.8 Hz, ^4J(H$_4$,H$_6$) = 1.0 Hz, ^3J(H$_5$,H$_6$) = 8.3 Hz
^{13}C: 14.4 (t, 14.4 Hz, P(*C*H$_3$)$_3$), 25.7 (C(O)*C*H$_3$), 197.6 (*C*(O)CH$_3$), 244.0 (t, 3.6 Hz, W-*C*O), 171.0 (C1), 122.6 (C2), 132.3 (C3), 114.7 (C4), 136.9 (C5), 125.1 (C6)
^{31}P: −9.73 (^1J(^{31}P,^{183}W) = 309 Hz)



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^{1}H: 1.30 (t, 3.4 Hz, P(C*H*$_3$)$_3$), 6.47 (d × d × d, H$_4$), 6.58 (d × d, H$_6$), 7.70 (d × d, H$_3$), 7.23 (d × d × d, H$_5$), 3.99 (s, C(O)OC*H*$_3$), ^3J(H$_3$,H$_4$) = 8.2 Hz, ^4J(H$_3$,H$_5$) = 1.9 Hz, ^3J(H$_4$,H$_5$) = 6.8 Hz, ^4J(H$_4$,H$_6$) = 1.1 Hz, ^3J(H$_5$,H$_6$) = 8.7 Hz
^{13}C: 14.8 (t, 13.8 Hz, P(*C*H$_3$)$_3$), 53.3 (O*C*H$_3$), 171.0 (*C*(O)OCH$_3$), 245.6 (t, 3.3 Hz, W-*C*O), 172.1 (C1), 117.7 (C2), 131.0 (C3), 114.8 (C4), 136.5 (C5), 124.1 (C6)
^{31}P: −9.33 (^1J(^{31}P,^{183}W) = 309 Hz)

[a] Measured in C_6D_6 at 22 °C.

If more than 1 equiv of salicylaldehyde is reacted with **1**, the reaction takes a more complicated course. As the amount of salicylaldehyde increases, the conversion rate of **3a** to **3b** slows down, as is illustrated by the k_2 values (Table III). This is probably due to competitive intermolecular hydrogen bonding of **3a** with salicylaldehyde, retarding the intramolecular proton transfer and formation of intermediate A during the rearrangement.

Three new compounds could be identified in the reaction mixture, namely **3c**, **3d**, and α,2-dihydroxytoluene (saligenin) (see Scheme II and Table IV),[14] whereas **3a** and **3b** eventually are both consumed. The isomeric tungsten salicylates **3c** and **3d** are formed by substitution of the alkoxy and phenoxy moieties in **3a** and **3b**, respectively, by excess salicylaldehyde, liberating in both cases α,2-dihydroxytoluene and carbon monoxide. Interestingly, compound **3c** is only formed as long as **3a** is present in the reaction mixture. This suggests that **3c** is selectively formed from **3a** and **3d** mainly from **3b**. Thus, during the isomerization of **3a** to **3b**, part of the presumed intermediate A is "trapped" by salicylaldehyde (probably by initial coordination of the aldehyde oxygen trans to the NO ligand to tungsten), forming **3c**. When **1**, **3a**, and **3b** are all consumed (a few hours at 22 °C), **3c**/**3d** can be isolated in 85% yield as an 8:92 isomer mixture, irrespective of the amount of salicylaldehyde.

Curiously, at higher salicylaldehyde/**1** ratios the rate of formation of **3d** (k_3; see Table III) is only dependent on the concentration of **3b** and is independent of the salicylaldehyde concentration.[15] This is characteristic of a pseudo-first-order reaction, indicating a dissociative mechanism for this substitution reaction. With regard to the observed lability of CO ligands in tungsten(0) alkoxy/phenoxy compounds, it is likely that the substitution of salicylaldehyde takes place by the rate-determining dissociation of a CO ligand from **3b**. Subsequent coordination of a salicylaldehyde molecule through the aldehyde oxygen atom to the tungsten center and subsequent proton transfer then affords the chelate complex **3d** and α,2-dihydroxytoluene.

Table V. Selected Bond Lengths (Å) for 3d

W-P(1)	2.474 (3)	O(3)-C(2)	1.26 (1)
W-P(2)	2.469 (3)	O(4)-C(8)	1.34 (1)
W-O(3)	2.158 (7)	C(2)-C(3)	1.39 (1)
W-O(4)	2.111 (7)	C(3)-C(4)	1.43 (2)
W-N	1.807 (9)	C(3)-C(8)	1.44 (1)
W-C(1)	1.95 (1)	C(4)-C(5)	1.34 (2)
(P-C)$_{av}$	1.81 (1)	C(5)-C(6)	1.43 (2)
O(2)-N	1.20 (1)	C(6)-C(7)	1.35 (2)
O(1)-C(1)	1.16 (2)	C(7)-C(8)	1.40 (1)

Table VI. Selected Bond Angles (deg) for 3d

P(1)-W-P(2)	174.6 (1)	O(4)-W-N	176.0 (3)
P(1)-W-O(3)	89.2 (4)	O(4)-W-C(1)	94.1 (4)
P(1)-W-O(4)	87.0 (2)	N-W-C(1)	89.9 (4)
P(1)-W-N	83.8 (4)	(W-P-C)$_{av}$	115 (3)
P(1)-W-C(1)	89.2 (4)	(C-P-C)$_{av}$	103 (1)
P(2)-W-O(3)	89.4 (2)	W-O(3)-C(2)	130.2 (7)
P(2)-W-O(4)	87.6 (2)	W-O(4)-C(8)	132.2 (6)
P(2)-W-N	92.2 (3)	W-N-O(2)	176.5 (8)
P(2)-W-C(1)	91.4 (4)	W-C(1)-O(1)	178 (1)
O(3)-W-O(4)	82.9 (3)	O(3)-C(2)-C(3)	127 (1)
O(3)-W-N	93.1 (3)	C(2)-C(3)-C(4)	117.6 (9)
O(3)-W-C(1)	176.9 (4)	O(4)-C(8)-C(3)	122.3 (8)

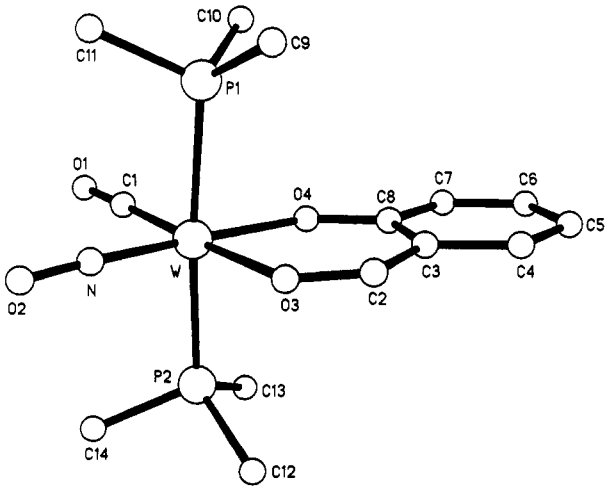
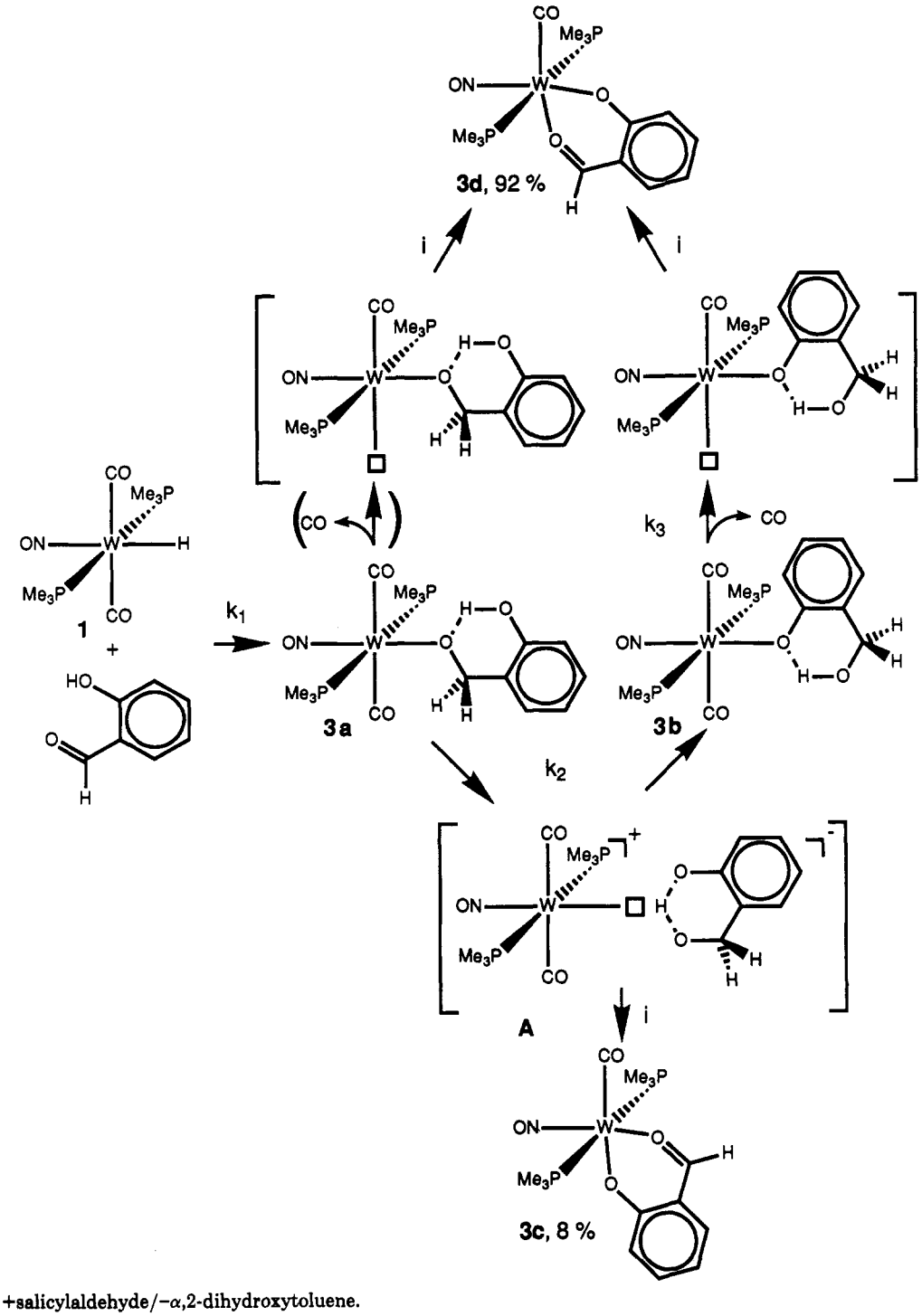


Figure 1. Molecular structure of **3d**. H atoms have been omitted for clarity.

(14) Since **3c** is present in only trace amounts, compared to the amount of **3d**, it could not be identified with absolute certainty. We notice, however, that the spectroscopic features which could be measured are very similar to those of the isomer **3d**: ^{1}H NMR (C_6D_6) δ 0.98 (t, 3.4 Hz, P(CH$_3$)$_3$), 8.50 (s, aryl-C(O)H); ^{31}P NMR (C_6D_6) δ −8.69 (s with 14% ^{183}W satellites, ^1J(^{31}P,^{183}W) = 307 Hz). Data for **3d** are given in Table IV and in the Experimental Part. Data for 2-(HOCH$_2$)C$_6$H$_4$OH: ^{1}H NMR (C_6D_6) δ 4.63 (s, aryl-CH$_2$OH), aromatic signals hidden; ^{13}C NMR (C_6D_6) δ 63.9 (aryl-CH$_2$OH), 116.6, 119.8, 126.0, 128.2, 129.1, 157.1.

(15) This is corroborated by the fact that the value of k_3 calculated from the appearance of **3d** matches k_3 calculated from the disappearance of **3b**.

Scheme II



[a] Legend: (i) +salicylaldehyde/−α,2-dihydroxytoluene.

When 5 equiv of salicylaldehyde was added to a solution of 1 in CD_3OD, no significant differences in the reaction sequence ocurred, as compared to that in C_6D_6. However, an estimated 5–10-fold increase of all reaction rates was observed. Obviously, methanol assists the proton transfer involved in most reaction steps but also helps to stabilize the various, polarized transition states by solvation.

Solid-State Structure of 3d. A definitive characterization of **3d**, especially concerning the position of the CO and NO ligands, was achieved by a single-crystal X-ray diffraction study. Selected bond distances and angles are summarized in Tables V and VI, respectively; the molecular structure of the compound is shown in Figure 1.

The molecule resides as a discrete monomer in the monoclinic crystal lattice, having an only slightly distorted octahedral geometry around the tungsten center. The structure confirms that the CO ligand is trans to the aldehyde oxygen, whereas the NO ligand is positioned trans to the phenoxy oxygen of the anionic salicylaldehyde moiety. All of these ligands lie on a noncrystallographic mirror plane, with the two phosphine ligands being almost perpendicular to it (∠P(1)–W–P(2) = 174.6 (1)°). Bond distances around tungsten are within the range of expected values.[4,16] The salicylate moiety, however, shows some anomalies. For example, the aldehyde bond O(3)–C(2) is somewhat longer (1.26 (1) Å) than a prototype >C=O distance (1.22 Å),[17] whereas the phenoxy bond O(4)–C(8)

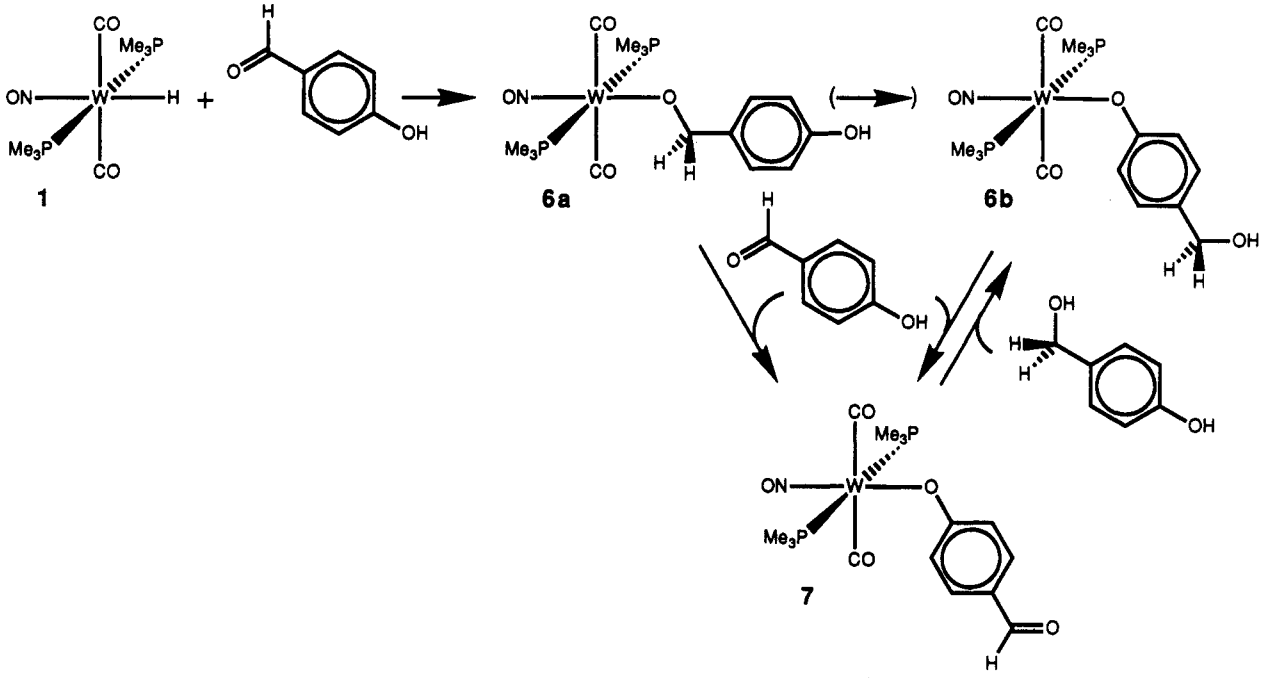
(16) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

Table VII. Geometrical Data for Salicylate Complexes[a]

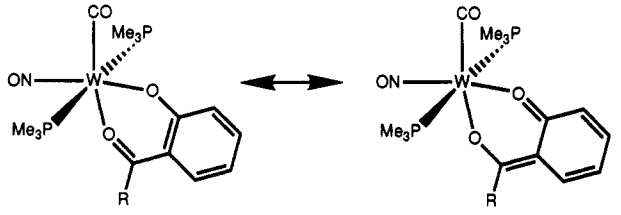
compd	O(3)–C(2)	C(2)–C(3)	C(3)–C(8)	O(4)–C(8)	C(3)–C(4)	C(4)–C(5)	C(5)–C(6)	C(6)–C(7)	C(7)–C(8)	ref
3d	1.26 (1)	1.39 (1)	1.44 (1)	1.34 (1)	1.43 (2)	1.34 (2)	1.43 (2)	1.35 (2)	1.40 (1)	this work
$Cu(sal)_2$, form A	1.26	1.39	1.45	1.32	1.39	1.36	1.43	1.31	1.43	18
$Cu(sal)_2$, form B	1.28	1.40	1.39	1.32	1.43	1.41	1.40	1.37	1.44	19
$[Cu(sal)(bpy)]ClO_4$	1.256 (5)	1.420 (6)	1.422 (5)	1.316 (4)	1.417 (6)	1.368 (7)	1.387 (7)	1.382 (6)	1.405 (5)	20
$[Cu(sal)(phen)]NO_3$	1.254 (4)	1.409 (6)	1.428 (5)	1.302 (4)	1.421 (5)	1.355 (6)	1.389 (7)	1.370 (6)	1.400 (5)	21
"ideal" sal ligand	1.22	1.49	1.39	1.37	1.39	1.38	1.38	1.38	1.38	17

[a] Abbreviations: sal = salicylate; bpy = 2,2′-bipyridyl; phen = 1,10-phenanthroline. The bond-numbering system refers to that of the X-ray structure of **3d**. All bond distances are given in Å.

Scheme III

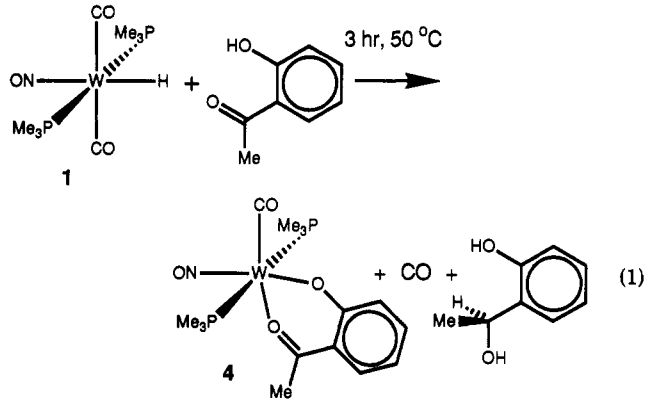


and the C(2)–C(3) bonds are shorter (1.34 (1) and 1.39 (1) Å) than expected (1.37 and 1.49 Å).[17] We attribute this to a mesomeric effect:



Similar resonance phenomena can be found in a series of copper(II) salicylate compounds, the important structural data of which are shown in Table VII. In our compound **3d**, we attribute this effect to the strong π-accepting properties of the NO ligand, which favors the quinoid resonance form, due to a support of conjugative donation of π-electrons from the trans-positioned sp^2 oxygen atom.

Related Reactions. Under more forcing conditions as for salicylaldehyde, 2-hydroxyacetophenone reacts with **1**. Two equivalents or more of the ketone is required to drive the reaction to completion. The isolable chelate complex **4** (Table IV) and equimolar amounts of the reduced product 1-(2-hydroxyphenol)ethanol[22] are the only products observed (eq 1).



(1)

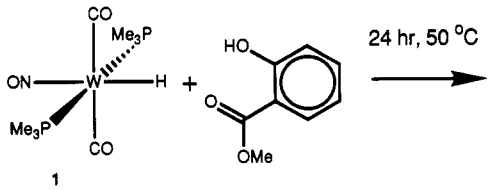
In contrast to the reaction of salicylaldehyde, no intermediate products analogous to **3a** and **3b** were observed. Although **4** consists principally of one isomer (probably structurally analogous to **3d**), small signals in the ^1H (1.90 ppm) and ^{31}P NMR spectra (−8.71 ppm) may be assigned to an isomer with CO/NO-exchanged ligand positions (ca. 3% abundance).

The reaction of **1** and methyl salicylate yields the chelate complex **5** (Table IV; eq 2). However, in contrast to the

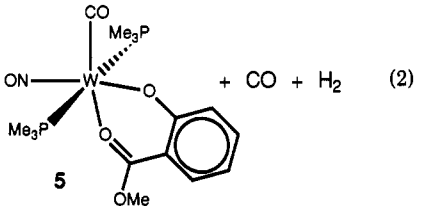
(17) Allen, H. A.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1987**, S1.
(18) McKinnon, A. J.; Waters, T. N.; Hall, D. *J. Chem. Soc.* **1965**, 3290.
(19) Hall, D.; McKinnon, A. J.; Waters, T. N. *J. Chem. Soc.* **1965**, 425.
(20) Garland, M. T.; le Marouille, J. Y.; Spodine, E. *Acta Crystallogr.* **1986**, *C42*, 1518.
(21) Solans, X.; Ruiz-Ramirez, L.; Brianso, J. L. *Acta Crystallogr.* **1987**, *C43*, 426.

(22) 1-(2-Hydroxyphenyl)ethanol: ^1H NMR (C_6D_6) δ 1.36 (d, 6.6 Hz, 3 H, $C(H)(OH)CH_3$), 4.75 (q, 6.6 Hz, 1 H, $C(H)(OH)CH_3$), 6.75 (m, 2 H), 7.05 (m, 2 H).

aforementioned cases, we do not observe reduced organic products, and we assume therefore that in this case dihydrogen is eliminated by a simple acid–base reaction.



1



5 (2)

The reaction of 1 with 4hydroxy-benzaldehyde in C_6D_6 was studied by ^1H NMR spectroscopy (Scheme III). As for salicylaldehyde, insertion takes place within minutes at room temperature, affording **6a** as the primary product.[23] From that stage on, the reaction course differs from that of salicylaldehyde, since a direct intramolecular isomerization of **6a** to the more stable phenoxy-bound isomer **6b** (cf. **3a** to **3b** conversion) is now geometrically inaccessible. As the main reaction path alternative, we observe the substitution of the alkoxy moiety of **6a**, by a second equivalent of 4-hydroxybenzaldehyde, producing **7** and α,4-dihydroxytoluene.[23] Then, **6b** is formed nevertheless, but in this case mainly by reaction of **7** with the phenoxy group of free α,4-dihydroxytoluene. Finally after a few hours, an equilibrium sets in between **7** and α,4-dihydroxytoluene on the one hand and between **6b** and 4-hydroxybenzaldehyde on the other. Obviously, a chelate effect as for the formation of **3d**, which could drive the reaction to the side of **7**, is not effective in the present case. Only after a large excess of 4-hydroxybenzaldehyde was added to the reaction mixture was the equilibrium shifted to this side.

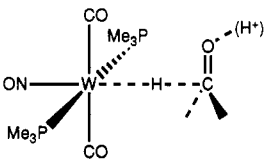
(23) ^1H NMR (C_6D_6): compound **6a**, δ 1.24 (t, 3.7 Hz, 18 H, $P(CH_3)_3$), 4.55 (s, 2 H, CH_2OW), 7.20 (d, 8.5 Hz, 2 H, aryl H's), 7.26 (d, 8.5 Hz, 2 H, aryl H's); compound **6b**, δ 1.18 (t, 3.6 Hz, 18 H, $P(CH_3)_3$), 4.40 (s, 2 H, CH_2OH), 6.60 (d, 8.4 Hz, 2 H, aryl H's), 7.12 (d, 8.4 Hz, 2 H, aryl H's); compound **7**, δ 1.09 (d, 3.7 Hz, 18 H, $P(CH_3)_3$), 6.44 (d, 8.7 Hz, 2 H, aryl H's), 7.67 (d, 8.7 Hz, 2 H, aryl H's), 9.76 (s, 1 H, aryl-C(O)H; 4-$(HOCH_2)C_6H_4OH$, δ 4.31 (s, 2 H, CH_2OH), 6.76 (d, 8.5 Hz, 2 H, aryl H's), 7.06 (d, 8.5 Hz, 2 H, aryl H's).

(24) (a) Darensbourg, D. J. In *Enzymatic and Model Carboxylation and Reduction Reactions for Carbon Dioxide Utilization*; Aresta, M., Schloss, J. V., Eds.; Kluwer: Dordrecht, The Netherlands, 1990; pp 43–64. (b) Sullivan, B. P.; Meyer, T. J. *Organometallics* **1986**, *5*, 1500. (c) Bo, C.; Dedieu, A. *Inorg. Chem.* **1989**, *28*, 304.

Conclusions

Aldehydes readily insert into the tungsten–hydride bond of **1** under mild conditions. The presence of an acidic phenoxy group in the system, either intermolecular as in phenol or intramolecular as in *o*- or *p*-hydroxybenzaldehyde, accelerates these insertions considerably. All of the primary alkoxy products are unstable with respect to CO loss and could therefore not be isolated. When possible, the tungsten alkoxides are substituted by a phenoxy group, affording more stable, but still not isolable, tungsten phenolates. Only if these phenolates contain additional functionalization, capable of forming a chelate ring with the tungsten center, may stable products be isolated (e.g. **3c,d** and **4**).

For the present insertion reactions of C=O double bonds into the W–H bond of **1**, we favor a mechanism that has been proposed for the insertion of CO_2 and M–H bonds[2b,9b,24] and that would be in agreement with the observed second-order kinetics. A direct nucleophilic attack of the hydride atom at the electrophilic C atom of the aldehyde is anticipated, and thus precoordination of the aldehyde to the metal center is not essential. A Brønsted acid, in this scheme, can coordinate to the O atom of the C=O double bond and thus enhances the electrophilicity of the C atom and accelerates the insertion:



We are currently investigating the reactivity of **1** with other aldehydes and ketones containing appropriate functional groups that can trap the primary alkoxy insertion products.

Acknowledgment. We thank the Swiss National Science Foundation for financial support.

Registry No. **1**, 136576-09-5; **2b**, 140677-60-7; **3a**, 140677-61-8; **3b**, 140696-62-4; **3c**, 140677-55-0; **3d**, 140850-83-5; **4c**, 140850-84-6; **4d**, 140677-56-1; **5**, 140677-57-2; **6a**, 140677-64-1; **6b**, 140677-63-0; **7**, 140677-62-9; *trans,trans*-$W(OPr)(CO)_2(NO)(PMe_3)_2$, 140696-61-3; *trans,trans*-$W(OCH_2Ph)(CO)_2(NO)(PMe_3)_2$, 140677-58-3; *trans,trans*-$W(OPh)(CO)_2(NO)(PMe_3)_2$, 140677-59-4; propanol, 71-23-8; benzyl alcohol, 100-51-6; salicylaldehyde, 90-02-8; α,2-dihydroxytoluene, 90-01-7; α,4-dihydroxytoluene, 623-05-2.

Supplementary Material Available: Tables of positional and thermal parameters and complete lists of bond lengths and angles (5 pages). Ordering information is given on any masthead page.

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